Evaluation of Fluorapatite as a Waste-Form Material

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Evaluation of Fluorapatite as a Waste-Form Material

(Task 16 for Third Year Renewal)

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TRP Research Area:  
Separations

Funding Profile:  

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Abstract:

Fluorapatite, fluorinated calcium phosphate, has been identified as a potential matrix for the entombment of the zirconium fluoride fission product waste stream from the proposed FLEX process. If the efficacy of fluorapatite-based waste-storage can be demonstrated, then new and potentially more-efficient options for handling and separating high-level wastes, based on fluoride-salt extraction, will become feasible. This proposal is for renewal of the UNLV portion of a dual-path research project to develop a process to fabricate a synthetic fluorapatite waste form for the ZrF₄, FP waste stream, characterize the waste form, examine its performance under environmental conditions, and correlate the behavior of the waste form with natural analogs. At UNLV, characterization of the material will be accomplished by probing molecular-scale electronic and geometric structure of the materials in order to relate them to macroscopic properties, with the goal of developing techniques to evaluate and predict the performances of different waste-form materials. Time and funding permitting, other waste forms for the zirconium fluoride, fission product salt waste stream will be examined and benchmarked against the fluorapatite matrix baseline.
Work Proposed for Academic Year 2004-2005 (8/04 – 7/05), Goals, and Expected Results:

The work in the third year of the project will continue to progress along two parallel paths: Fabrication and Natural-Analog Characterization. The Fabrication path, led by the KRI team, will evaluate various techniques for the fabrication of synthetic fluorapatite, will synthesize fluorapatite, and will begin the examination of waste loading and fabrication process factors on the synthetic fluorapatite. The Characterization path, led by the UNLV team, has been performing baseline spectroscopic studies of natural and pristine (no artificially added impurities) apatite materials and is beginning to apply the same techniques to more-complex fluorapatite-based waste forms made by the KRI Fabrication team. The ultimate goal is to use these techniques to achieve a molecular-level understanding of natural fluorapatite and other fluoride-bearing phases as natural analogs for waste-form materials. These techniques will also be used to examine changes in surface chemistry caused by environmental degradation.

Background and Rationale:

One of the more promising transmutation strategies currently proposed is the dual-strata approach in which plutonium is separated from the minor actinides and burned in reactors while the minor actinides are transmuted using an accelerator-driven system. This method allows energy value to be recovered from the plutonium and reduces the throughput requirements and complexity of the accelerator-driven transmutation system, which would have a smaller volume of material to handle and would not need to provide electricity for the grid.

Among technologies under consideration for the plutonium-burning reactor systems are the new-generation High-Temperature Gas-Cooled (HTGR) reactor designs, such as the Pebble-Bed Modular Reactor (PBMR) and the PRISM HTGR design. Among other attributes, both designs use a TRISO-coated fuel (a silicon-carbide and pyrocarbon composite coating). This fuel form is very stable and is one of the key components in the safety performance of these systems. However, TRISO-coated fuel is more difficult to recycle than other fuels under consideration. Because the plutonium-laden fuel in the second strata will need to be processed to recycle unburned plutonium and to recover for transmutation minor actinides and other fission products produced in the fuel cycle, it is essential the fuel is easily reprocessed. For this purpose, ANL has developed a new, fluoride-salt-based extraction procedure to handle TRISO-coated fuels known as the Fluoride Extraction, or FLEX, Process.

A potential problem with the FLEX process is the primary waste stream is a zirconium-fluoride (ZrF4) salt containing approximately 15 wt% fluoride salts of fission products (Cs, Sr, rare earths, etc.; composition of waste expected to be typical of fission products from commercial spent nuclear fuel; technetium). Fluoride salts are unsuitable for conversion into traditional borosilicate waste glass currently targeted for High-Level-Waste (HLW) disposal in a geological repository. The goal of this project is to develop a waste form for the disposal of this fission-product salt-waste stream, resolving the waste-stream management problem facing the FLEX process, and allowing the national spent-fuel management program to further examine, develop, and potentially deploy a promising new technology.

Research Objectives and Goals:

The research objectives are:

- To develop a waste matrix for the disposal of the fission-product waste stream from the FLEX process
- To develop a process to make synthetic fluorapatite that incorporates the FP-bearing ZrF4 salt
- To develop a fundamental understanding of the chemistry of this new waste form in order to better predict its long term behavior in a repository environment
- To develop a fundamental understanding of natural, fluoride-bearing mineral phases to use as natural analogs to bound the predicted behavior of the FLEX fission product waste stream

The goals are:

- To provide a level of understanding of the chemistry involved in the corrosion/dissolution of fluoride-bearing minerals and waste forms
- To develop experience with and a base of knowledge for the fabrication of fluoride-bearing matrices
- To develop a knowledge base to assist others in predicting the impact the FLEX process waste will have on the performance of a HLW repository
Technical Impact:

The proposed work will contribute to the fields of waste management and materials science through the development and characterization of the fabrication, molecular structure, performance, and corrosion mechanisms of fluoride-containing minerals and ceramics. The waste matrices and fabrication processes developed and examined through this work will serve to reduce, or even eliminate, one of the major hurdles facing molten-salt fuel-processing strategies; i.e., how can the salt wastes be stabilized for disposal. The characterization effort will expand our understanding of molecular structure of fluorapatite and other fluoride-bearing mineral and ceramic phases, and will deepen our understanding of bulk and surface processes during environmental degradation of these materials.

Research Approach:

The research to develop and understand a fluorapatite-based waste matrix for the ZrF₄-salt fission-product waste stream from the FLEX process will take place along two parallel paths: waste-form development, and waste-form characterization. The waste-form-development work will take place primarily at the Khlopin Radium Institute, and will be led by the KRI Principal Investigator, Dr. Rimsky-Korsakov. It is described in a separate proposal. The waste-form-characterization work will take place primarily at UNLV and using UNLV x-ray facilities at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL). The characterization work is led by PI Lindle and co-PI Hemmers.

Results from Year 2

Work at UNLV in Year 2 of the project focused in part on applying x-ray spectroscopy and more-conventional characterization techniques (e.g., FTIR, SEM, XRD, Raman spectroscopy) to natural crystals of apatite and fluorapatite and commercially available hydroxyapatite powder in order to obtain baseline measurements of these “pure” materials. The need for baseline measurements stems from the nearly complete lack of published work on these materials using molecular-scale characterization methods; before applying such techniques to waste-form materials, we must first understand the basic backbone material(s) of the waste-form matrix. Several examples of such data are shown below. A second focus in the past year was to test chemical methods for incorporating surrogate metals (Zn, Sr) into apatite materials. These metal-containingapatites and fluorapatites were then studied with the same cadre of characterization techniques noted above to assess the degree of incorporation and any changes in the physical and chemical structure of the materials. This work is partly a prelude to probing real waste-form materials provided by our KRI collaborators, in order to perfect the methods to be used, and partly to better understand the solid-state chemistry of apatite materials. The following section includes a summary of the work performed in the past year.

Solid State Synthesis of Zn Containing Fluorapatite

Over the past year we adopted methods to synthesize fluorapatite in the lab at UNLV and our first studies focused on Zn contained in Fluorapatite. A stoichiometric mixture of CaF₂ (powder) + ZnO + Ca₅(PO₄)₃OH (HAp or Hydroxyapatite) was heated to 1200°C in air for 7 hours. The product was analyzed using photoacoustic IR spectra and SEM micrographs. Figure 1 shows the changes observed in IR absorption bands of phosphate vibration and bending modes. It is clear there is a definite shift in the peak position around 1025 cm⁻¹ and 1100 cm⁻¹ and also there is a peak at 935 cm⁻¹, which was not observed in the reaction mixture. Separation of unreacted CaF₂ from the main product proved to be a problem.
Reflux Method Synthesis of Strontium containing Hydroxyapatite

<table>
<thead>
<tr>
<th>Mixture ratio (moles)</th>
<th>Refluxing hours</th>
<th>Figure Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excess SrCl₂ : HAp</td>
<td>24</td>
<td>Figure 2</td>
</tr>
<tr>
<td>(SrCl₂) 1:1 (HAp)</td>
<td>24</td>
<td>Figure 3</td>
</tr>
</tbody>
</table>

The reflux method is used to synthesize Sr containing hydroxyapatite and the mixtures shown in the table above were refluxed in aqueous medium at 100°C. Then the product was filtered out and rinsed with distilled water to remove unreacted SrCl₂ remain in the mixture. Then the solid powder dried in a desiccator and in a vacuum oven. Then SEM micrographs were obtained for both samples.

It can be seen in figure 2 that after the reflux with an excess strontium ion concentration, the powder material becomes more amorphous and less crystalline. The stability of the crystal structure of apatite is one of the key factors for its thermal stability and low solubility in aqueous medium.
We then changed the mixture ratio to 1:1 for the solutions of strontium ions and HAp which were then refluxed. The results turned out to be quite different from the previous ratio and are shown in figure 3.

![SEM micrograph obtained for 1:1 solutions of Strontium ions and HAp solutions.](image)

Figure 3. SEM micrograph obtained for 1:1 solutions of Strontium ions and HAp solutions.

Two different phases have been observed in the SEM micrographs. One phase closely resembles the SEM micrographs obtained for pure HAp. The second phase has a different morphology as can be seen in figure 3. It may be a that a new phase developed over the hydroxyapatite grains or that a new phase formed during the reflux process. EDS (Energy Dispersive Spectra) were obtained on the surfaces and elemental analysis was done.

<table>
<thead>
<tr>
<th>Element</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>41.34</td>
</tr>
<tr>
<td>P</td>
<td>27.8</td>
</tr>
<tr>
<td>Cl</td>
<td>0.03</td>
</tr>
<tr>
<td>Ca</td>
<td>13.21</td>
</tr>
<tr>
<td>Sr</td>
<td>16.72</td>
</tr>
</tbody>
</table>

Table 1. Elemental percentages (approximately) on the surface of newly observed phase.

**Thermal stability of apatites with different calcium to phosphorous molar ratios**

After studying the incorporation of Zn into the apatite structure using refluxing methods we were interested in how the Ca/P molar ratio of the prepared samples changes for different Zn concentrations. We compared those to results obtained for some other samples synthesized using same initial Ca:Zn weight ratios without refluxing.

Characterization of these samples was performed using spectroscopic methods such as x-ray photoelectron spectroscopy (XPS), infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Elemental analyses of these samples were done using atomic absorption spectroscopy (AAS) and the study of their thermal behavior was done using thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC).

**Experiment and Instrumentation**

**Synthesis**

A mixture of synthetic hydroxyapatite and 0.2M Zn$^{2+}$ solution was refluxed using water as the solvent for about 24 hours at 100°C. The set up that was used is similar to the following one. As an initial step a mixture of
hydroxyapatite and excess ZnCl\(_2\) was refluxed at 100\(^\circ\)C for about 7 hours. Further, three other samples with different initial Ca/Zn weight ratios were synthesized by refluxing 24 hours at the same temperature. Other than these four samples, another three samples with the same initial Ca/Zn weight ratios as in last three samples were synthesized without refluxing. These were prepared in order to see any type of crystals that would form in a system that does not disturb the crystallization.

**Characterization of samples**

The as synthesized samples were characterized using different spectroscopic methods. Elemental analysis was done using atomic absorption spectroscopy and the structural studies were done using infrared spectroscopy, x-ray photoelectron spectroscopy and energy dispersive spectroscopy. Scanning electron spectroscopy was used to examine the morphology of the samples. Thermal behavior of them was examined by means of thermo gravimetric analysis and differential scanning calorimetric profiles.

**Results and data analysis**

**Elemental Analysis**

The following table summarizes the determined elemental data of few samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Used Ca:Zn (w:w)</th>
<th>Determined weights in 1g of the sample</th>
<th>Molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ca</td>
<td>P</td>
</tr>
<tr>
<td>Hr11</td>
<td>1:1</td>
<td>0.16</td>
<td>0.18*</td>
</tr>
<tr>
<td>Hr105</td>
<td>1:0.5</td>
<td>0.18</td>
<td>0.18*</td>
</tr>
<tr>
<td>Hr1025</td>
<td>1:0.25</td>
<td>0.33</td>
<td>0.18*</td>
</tr>
<tr>
<td>Hap</td>
<td>1:0</td>
<td>0.39*</td>
<td>0.18*</td>
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</table>

*: These values are determined assuming Stoichiometry of hydroxyapatite.

Table. 2 Elemental data of different samples

The Ca levels in these samples are increased with the decrease in used Zn levels. The same kind of trend can be seen in the Ca/P molar ratios. For Zn, a decrease of its concentration in these samples can be identified in correlation with a decrease in Zn concentrations used in preparing the samples. This implies that Zn is incorporated in the structure. For the first two samples the Ca/P molar ratios are very low. For 1:0.25 initial Ca:Zn weight ratio the sample has a molar ratio of 1.42 for Ca/P. This value is very close to that of the stoichiometric value of hydroxyapatite. Thus it is important to use initial Zn levels of less than 1:0.25 to prepare samples with a Ca/P molar ratio close to that of hydroxyapatite.

**X-ray Photoelectron Spectroscopic (XPS) data**

With the help of XPS analysis we identified the elements, which are present in the different samples as well as their different oxidation states. For a hydroxyapatite sample Ca, P and O are the main elements that can be identified (Fig 4). For O the 1s oxidation state is prominent and for P the states 2s and 2p, 2s, 2p, 3s and 3p are the main oxidation states of Ca in hydroxyapatite. Except for a few elemental oxidation states the lowest binding energies can be seen in the original hydroxyapatite sample (Table 3). This indicates that there is some kind of interface interaction in the Zn-containing hydroxyapatite samples.
Table 3 Binding energies of elements in different samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>C 1s</th>
<th>Ca 2p</th>
<th>O 1s</th>
<th>P 2p</th>
<th>Zn 3p</th>
</tr>
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<tbody>
<tr>
<td>Hr11</td>
<td>284.60</td>
<td>346.80</td>
<td>530.30</td>
<td>132.16</td>
<td>89.17</td>
</tr>
<tr>
<td>Hr105</td>
<td>284.60</td>
<td>346.68</td>
<td>530.73</td>
<td>132.36</td>
<td>88.90</td>
</tr>
<tr>
<td>Hr1025</td>
<td>284.60</td>
<td>347.03</td>
<td>530.88</td>
<td>132.45</td>
<td>88.13</td>
</tr>
<tr>
<td>Hap</td>
<td>284.59</td>
<td>346.36</td>
<td>530.47</td>
<td>132.16</td>
<td>-</td>
</tr>
</tbody>
</table>

**Energy Dispersive Spectroscopic (EDS) data**

Data obtained from energy dispersive spectroscopy of the samples has similar features as the data obtained from XPS. Mainly the presence of different elements in their different oxidation states of the samples can be identified. Zn can be seen in all synthesized samples (Fig. 5).
Scanning Electron Microscopic (SEM) data

Analysis of SEM micrographs is an excellent method of studying the morphology of samples. The micrographs of hydroxyapatite with different magnifications are shown in Fig 6. The micrograph on the left side of Fig 6 shows how the morphology of synthetic hydroxyapatite looks like. From the magnified micrograph on the right side of Fig. 6 it can be clearly seen that the particles are thin and long like needles.

The micrographs of the other four samples are shown in Fig 7. Basically, the morphology has been changed with the increase of Zn levels in these samples. And they confirm the incorporation of Zn to the hydroxyapatite structure. In Fig 7 (a) and (b) the morphologies are more similar to that of hydroxyapatite than (c) and (d). But (a) and (b) show
some regions of clusters of particles which is more obvious in Fig 5 (b). For the sample that was synthesized using the 1:1 initial weight ratio of Ca:Zn (Fig 5 (c)) the particle shapes are not so clear and this sample is more amorphous than the other three samples. This reduced crystallinity of this sample may be due to the incorporation of Zn into the apatite structure in a higher level. This can also be seen from the elemental analysis data of this sample. The micrograph for the fourth sample (Fig 5 (d)) is much more different than the other three. Here the sample has different types of crystals. They can be thought of as loose, hexagonal, euhedral crystals and subhedral, hexagonal crystals. Other than these, there is a third kind that can be thought of as a surface, which may be identified as a crystallized surface of hydroxyapatite. The formation of these kinds of crystals may be due to homogeneous and heterogeneous crystallization.

![Fig. 7 SEM micrographs of synthesized samples with different initial Ca:Zn weight ratios, 1:0.25 (a), 1:0.5 (b), 1:1 (c), 1:6.5 (d)](image)

**Fourier Transform Infrared Spectroscopic (FTIR) data**

In the FTIR analysis, mainly the peaks for PO$_4^{3-}$ and OH$^-$ groups in the hydroxyapatite can be identified in Fig 8. Peaks at 482, 574-605, 964, 1033-1118 and 1226 cm$^{-1}$ have to be due to PO$_4^{3-}$. For the OH$^-$ group the peak positions are 636 and 3568 cm$^{-1}$. The peaks at 883 and 1654 cm$^{-1}$ may be due to HPO$_4^{2-}$ and H$_2$O while the peak at 2002 could be due to PO$_4^{3-}$ overtones.
For the other samples the main peak positions of PO₄³⁻ and OH⁻ groups can be seen almost at the same positions as for hydroxyapatite, except for the samples synthesized by refluxing and using 1:1 initial Ca:Zn weight ratio (Fig 9). This is accordance with its reduced crystallinity and can be thought of as structure of apatite that remains after the incorporation of Zn.

**Thermal behavior of Zn-containing hydroxyapatite**

The TG/DSC profiles for the two samples are shown in Figs. 10 and 11. The TG in Fig. 10 shows the thermal behavior of hydroxyapatite in the temperature range between 30°C and 510°C. Only one weight loss at around 200°C can be seen. This weight loss is due to the removal of water adsorbed on to the surface of the sample. Therefore, an endothermic peak is observed in the DSC plot at this same temperature.

Zn-containing hydroxyapatite shows a number of weight losses (Fig. 11). The two weight losses near 100°C and 325°C may be due to phase transitions, most probably due to phase dissolutions. The second weight loss at around 175°C may be due to the removal of water that adsorbed on to the surface of the sample as in case of hydroxyapatite. The three endothermic peaks in the DSC graph at those temperatures support these three weight losses.
**Fig. 10** TG/DSC profiles of Hap

**Fig. 11** TG/DSC profiles of Zn-containing Hap
Due to complications in setting up the subcontract between UNLV and the Khlopin Radium Institute, the contract for the work described in the Fabrication path was not initiated until May 2003. The first year’s work scope for this subcontract will continue in FY03, through May 2004.

Plans for Year 3

State-of-the-art x-ray spectroscopy and spectromicroscopy techniques will be employed to characterize molecular structure of both natural fluorapatite and fluoride-bearing minerals and the fluorapatite-based ceramic waste forms. Changes in the surface/interfacial chemistry of these materials as they undergo reactions with species in the environment also will be examined to help develop a basis for understanding corrosion chemistry the waste form and its natural analogs may experience under repository conditions. Inclusion of molecular-scale characterization of fluorapatite materials in the research approach is necessary to fully understand and predict macroscopic properties and functionality of the materials. Previous studies of fluorapatite using different types of spectroscopy and microscopy have demonstrated this approach yields data vital for predicting performance and integrity of a target compound. Molecular-based reaction mechanisms, crucial to the design of useful fluorapatite materials, have been devised for reactions and thermal stability of apatite and apatite-related materials as well as decomposition into mixtures of other products. It is now known very slight alterations in molecular composition of these materials affects stability, mechanical integrity, and other performance characteristics. As a result, a rigorous molecular-based understanding of apatites and their fluorinated derivatives is needed in order to properly model the materials and their applications.

To continue to move toward this overarching goal, work in Year 3 will finalize creation of the baseline spectroscopic information for both “pure” and selected metal-doped apatite materials, including detailed measurements with synchrotron-radiation-based x-ray techniques. With the powerful capabilities available at the ALS, we expect to be able to see components of natural crystals and waste-form materials hitherto unmeasurable with conventional techniques. All of this work will be a prelude to studying apatite materials incorporating wastes and waste surrogates fabricated by our KRI colleagues, providing a direct connection between molecular-scale understanding and waste-form processing. Finally, the chemistry of waste-form incorporation will continue to be studied at UNLV by performing a few ‘simple’ benchmark experiments under well-defined conditions; mixtures of well-characterized materials, both apatite and surrogate, will be chemically or physically prepared, then subjected to the same battery of spectroscopic techniques. The goal is to understand the structure of the resulting materials, as well as the specific chemical or physical processes by which they form. This information can then feed into spectroscopic studies of true waste-form materials, such as those to be fabricated at KRI.

Expected Technical Results:
- Development of a fluorapatite-based waste form for the FLEX process fission product waste stream
- Characterization of the molecular structure and corrosion behavior of natural fluorapatites
- Characterization of the molecular structure and corrosion behavior of fluorapatite-based waste forms
- Development of experimental techniques to predict the general efficacy of waste-form materials

Capabilities

UNLV and LBNL:

All of the equipment required for the proposed research is available to the PIs; no equipment request is being made to AAA as part of this proposal.

The UNLV PI has access to a variety of state-of-the-art instrumentation for materials research, including: (1) a stand-alone X-ray Photoelectron Spectroscopy (XPS) apparatus; (2) a Near-Edge X-ray Absorption Fine Structure (NEXAFS) chamber for mapping chemical structure of a sample with micron spatial resolution; and (3) two high-resolution X-ray Emission Spectroscopy (XES) instruments covering the ranges 100-800 eV and 2000-6000 eV, exactly the energy regions needed to probe the elemental species in fluorapatite samples. In the near future, the XPS analyzer in (1) will be adapted to apparatus (2) to allow micro-XPS experiments. Lindle also has preferred access to two high-resolution x-ray beamlines at the ALS, spanning the photon-energy range 100-6000 eV. This range includes core-level thresholds for all elements in the fluorapatite materials of interest (Ca, P, O, F, C) as well as in the waste materials (Cs, Sr, rare earths), allowing the full complement of x-ray techniques to be applied. Other
equipment is available at UNLV, such as an x-ray-diffraction system in the lab of Prof. Malcolm Nicol and a second, higher-spatial-resolution XPS apparatus housed at DRI.

We emphasize the necessity of using x-ray facilities at the ALS; it is a unique national asset with unparalleled x-ray flux, brightness, and beam collimation in the photon-energy range needed for this program. Quite simply, the proposed research cannot be fully accomplished without performing experimental work at the ALS. Despite partial reliance on the ALS national-user facility, it is important to realize existing UNLV efforts and instrumentation at the ALS are fully recognized by the relevant communities as components of UNLV research programs, rather than as DOE or LBNL programs; the ALS serves solely as a key tool, just as a research-quality laser might in physics experiments.

KRI

Since 1990 the Laboratory of Applied Mineralogy and Radiogeochemistry of V.G. Khlopin Radium Institute (KRI) has studied different types of crystalline host-phases for use as potential waste matrices, and for the immobilization of actinides for geological disposal. The lab has significant experience in waste form development, including the development of actinide (An)-doped ceramics based on the following host-phases: zircon [(Zr, An…)SiO₄], zirconia [(Zr, Hf, An…)O₂], monazite [(Ce, La, An…)PO₄], and garnet [(Y, Ca, An…)(Al…)₃O₁₂]. This unique expertise will allow the Applied Mineralogy group not only to develop a waste matrix for the ZrF₄-fission product salt waste stream, but will also prove vital in evaluating the process for use with highly radioactive solutions. If necessary, this experience will also allow for the inclusion of technetium and minor actinides to directly evaluate their impact on the waste matrix without needing to bring in additional collaborators. The Laboratory of Applied Mineralogy and Radiogeochemistry also has the experience and facilities to examine the material properties of these waste forms and to examine the leach resistance/environmental performance of the various compositions to be developed.

The following are the methods and equipment to be used in the research effort:

- Quantitative XRD analysis (using “Geiger-Flex” Rigaku XRD Spectrometer) to identify crystalline phases and their amounts in matrices of actinide-doped and non-radioactive ceramics. KRI developed the original method of precise XRD analysis for highly radioactive materials.
- The chain of glove boxes equipped with the following: ball mill, cold press, calcinations furnaces, and ceramic synthesis furnaces. These boxes are designed to handle up to 2 grams of ²³⁹Pu and 0.2 g ²³⁸Pu.
- Scanning electron microscopy (SEM) combined with microprobe analysis (EPMA) and cathodoluminescence (CL) spectrometry (using MS-46 Camebax with installed original CL-spectrometer) will be used to determine chemical composition of actinide host phases and separated actinide species. In some cases the CL method allows the determination of the valence state of the actinides and other elements incorporated by the crystalline materials.
- Special Teflon™ vessels and thermostatic ovens to perform MCC-1 leach tests of actinide-doped and non-radioactive ceramic samples.
- Optical microscopy (in reflected light) – using high-quality Russian microscope МИМ-10 equipped with digital photo camera – to observe visually the structural features (porosity, grain size, etc.) of actinide-doped ceramics.
- Fully licensed facility for working with the actinides at levels greater than 10 mCi.

Project Timeline:

Timeline Narrative

The timeline below describes expected technical results, milestones, and deliverables for Year 3. This project will contribute to the training of two graduate students. Not only will they become familiar with TRP-related science and technical issues, but they also will have an excellent opportunity to work at a DOE National Laboratory and a DOE-operated national user facility on an international collaborative effort.
Expected technical results for Year 3:

- Composition analyses of solid-state phases of fluorapatite and derivatives
- Spectroscopic studies of fluorapatite and derivatives, including some waste-loaded materials
- Initial studies of environmentally simulated reactions
- Initial studies of waste-loading in fluorapatite materials

Milestones for Year 3:

- Completion of baseline spectroscopic measurements for waste-free apatite and fluorapatite materials
- First detailed synchrotron-radiation-based x-ray measurement and analysis of apatite materials
- Initial studies of waste-loaded materials fabricated at KRI
- Preliminary studies of simple chemical and physical processes involved in waste incorporation

Deliverables for Year 3:

- **Collaboration with DOE:** Regular communication with DOE collaborator to assess progress, discuss problems, and allow for refocusing if necessary to address shifts in direction by the National Project.
- **Quarterly Progress Reports:** Brief reports indicating progress will be provided every quarter in support of the DOE AAA quarterly meetings.
- **Annual Report:** Written reports detailing experiments performed, data collected and results to date.

Data will be incorporated into student theses and peer-reviewed publications.